X-ray Emission Spectroscopy of 5f and Environmental Materials

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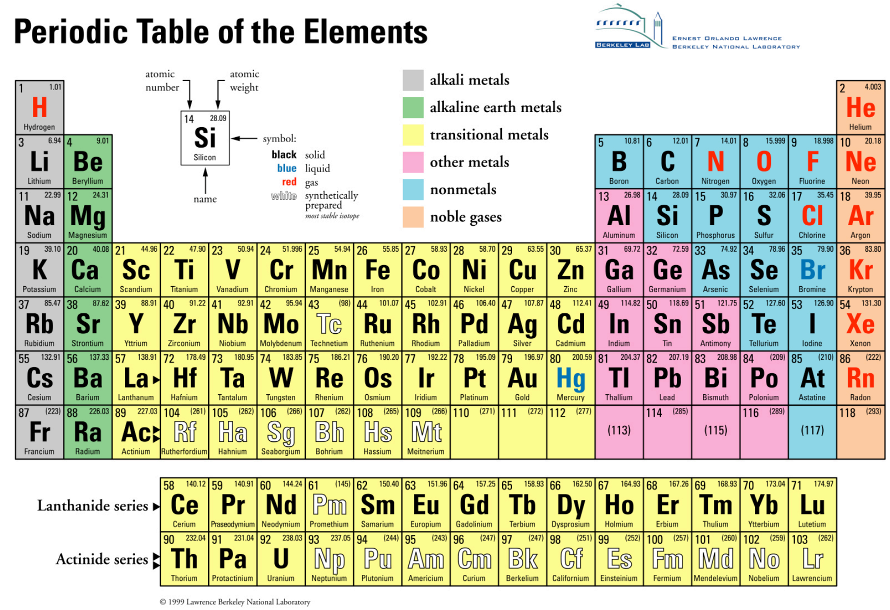
20 October 2004



Actinide Science and Interface Science with Tunable Soft X-rays

Understand the complex chemistry and physics of the actinides resulting from *5f* electron interactions

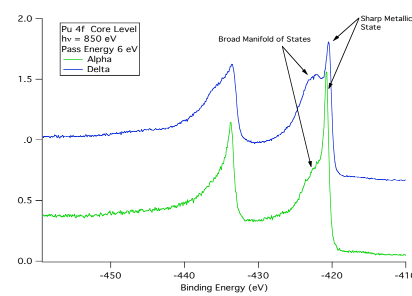
Surface/interface science, both traditional and modern; photoelectron, XAS, x-ray emission, [polarization]

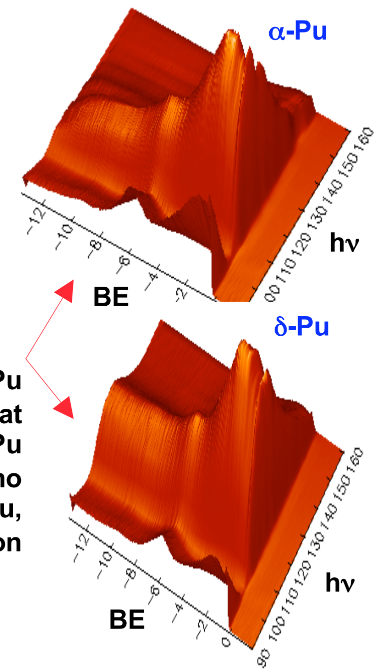
Soft x-rays probe the electronic structure of bonding orbitals (*5d*-*5f* transition ~100 eV)

Direct probe of light elements B, C, O, N, Al, Si plus others

Safety and sample preparation

Pu 4f Core Level Spectra





Fano-like line shapes for both. α-Pu shows structure in CIS line shape at Fermi edge while δ-Pu does not. δ-Pu spectrum shows greater Fano symmetry and larger q value than α-Pu, consistent with greater electron localization in δ-Pu.

J. Terry et al., Surf. Sci. **499**, 141 (2002)

J. G. Tobin et al., Phys. Rev. B **68**, 155109 (2003)

K. T. Moore et al., Phys. Rev. Lett. **90**, 196064 (2003)

Several MRS and other Proceedings

Spurred other work

Use of Radioactive Materials in the soft X-rays Region at the ALS

LBNL Tradition of Handling Radioactive Materials Safely

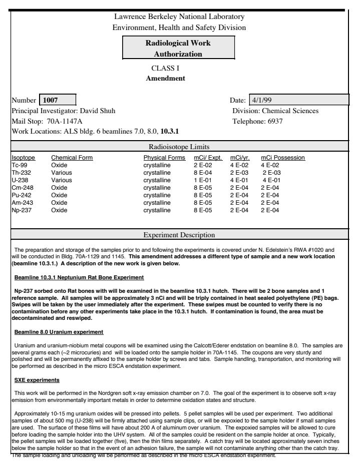
Partnership with LBNL Environment, Health & Safety

Graded Approach to Safety

Handling Radioactive Materials at the ALS

ALS Scientific Advisory Committee (2003)

Actinide Experiments at the ALS – 3 Categories



Lawrence Berkeley National Laboratory
Environment, Health and Safety Division

Radiological Work Authorization

CLASS I
Amendment

Number **1007** Date: 4/1/99
Principal Investigator: David Shuh Division: Chemical Sciences
Mail Stop: 70A-1147A Telephone: 6937
Work Locations: ALS bldg. 6 beamlines 7.0, 8.0, **10.3.1**

Radioisotope Limits

Isoptope	Chemical Form	Physical Forms	mCi/ Expt.	mCi/yr.	mCi Possession
Tc-99	Oxide	crystalline	2 E-02	4 E-02	4 E-02
Th-232	Various	crystalline	8 E-04	2 E-03	2 E-03
U-238	Various	crystalline	1 E-01	4 E-01	4 E-01
Cm-248	Oxide	crystalline	8 E-05	2 E-04	2 E-04
Pu-242	Oxide	crystalline	8 E-05	2 E-04	2 E-04
Am-243	Oxide	crystalline	8 E-05	2 E-04	2 E-04
Np-237	Oxide	crystalline	8 E-05	2 E-04	2 E-04

Experiment Description

The preparation and storage of the samples prior to and following the experiments is covered under N. Edelstein's RWA #1020 and will be conducted in Bldg. 70A-1129 and 1145. **This amendment addresses a different type of sample and a new work location (beamline 10.3.1.) A description of the new work is given below.**

Beamline 10.3.1 Neptunium Rat Bone Experiment

Np-237 sorbed onto Rat bones with will be examined in the beamline 10.3.1 hutch. There will be 2 bone samples and 1 reference sample. All samples will be approximately 3 nCi and will be triply contained in heat sealed polyethylene (PE) bags. Swipes will be taken by the user immediately after the experiment. These swipes must be counted to verify there is no contamination before any other experiments take place in the 10.3.1 hutch. If contamination is found, the area must be decontaminated and reswiped.

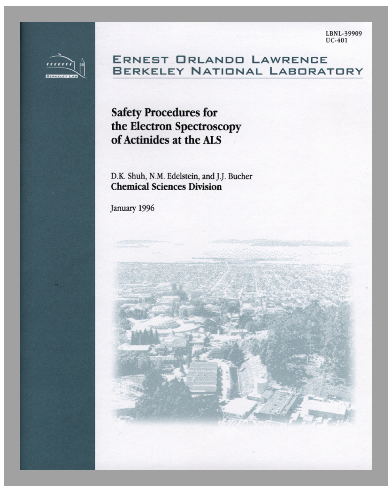
Beamline 8.0 Uranium experiment

Uranium and uranium-niobium metal coupons will be examined using the Calcott/Ederer endstation on beamline 8.0. The samples are several grams each (~2 microcuries) and will be loaded onto the sample holder in 70A-1145. The coupons are very sturdy and polished and will be permanently affixed to the sample holder by screws and tabs. Sample handling, transportation, and monitoring will be performed as described in the micro ESCA endstation experiment.

SXE experiments

This work will be performed in the Nordgren soft x-ray emission chamber on 7.0. The goal of the experiment is to observe soft x-ray emission from environmentally important metals in order to determine oxidation states and structure.

Approximately 10-15 mg uranium oxides will be pressed into pellets. 5 pellet samples will be used per experiment. Two additional samples of about 500 mg (U-238) will be firmly attached using sample clips, or will be expoxied to the sample holder if small samples are used. The surface of these films will have about 200 A of aluminum over uranium. The expoxied samples will be allowed to cure before loading the sample holder into the UHV system. All of the samples could be resident on the sample holder at once. Typically, the pellet samples will be loaded together (five), then the thin films separately. A catch tray will be located approximately seven inches below the sample holder so that in the event of an adhesion failure, the sample will not contaminate anything other than the catch tray. The sample loading and unloading will be performed as described in the micro ESCA endstation experiment.



LBNL-39909
UC-401

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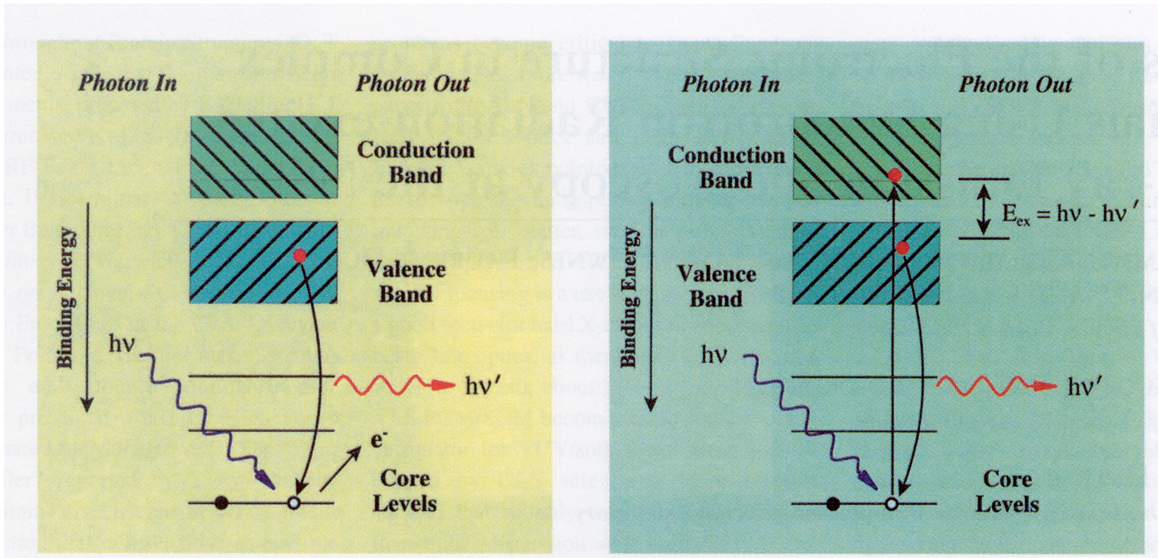
BERKELEY NATIONAL LABORATORY

Safety Procedures for the Electron Spectroscopy of Actinides at the ALS

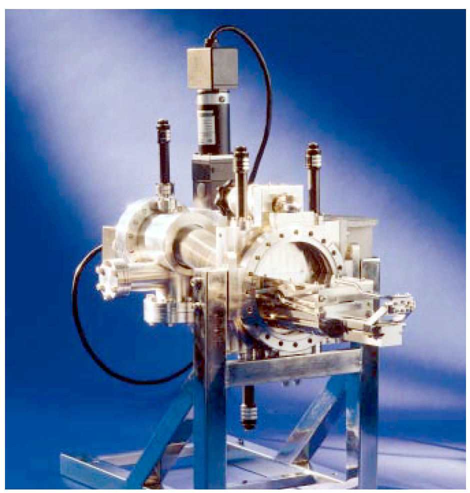
D.K. Shuh, N.M. Edelstein, and J.J. Bucher
Chemical Sciences Division

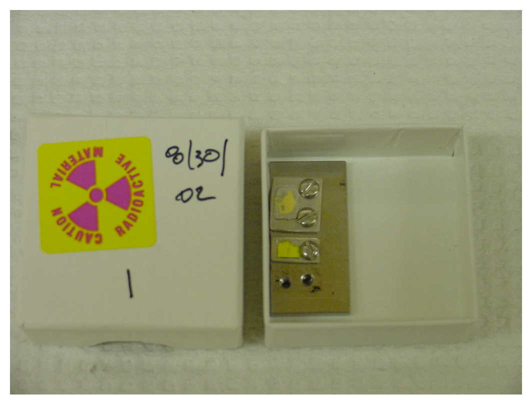
January 1996

Photon in, Photon out

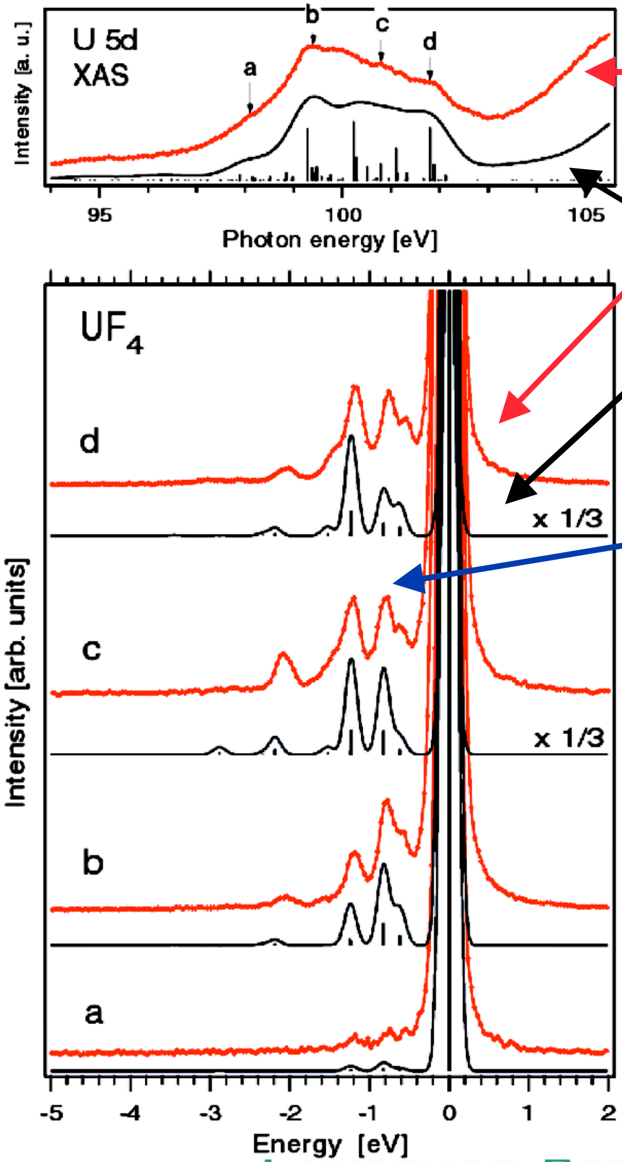


a) Soft X-Ray Emission b) Resonant Inelastic X-Ray Scattering





Uranium RIXS

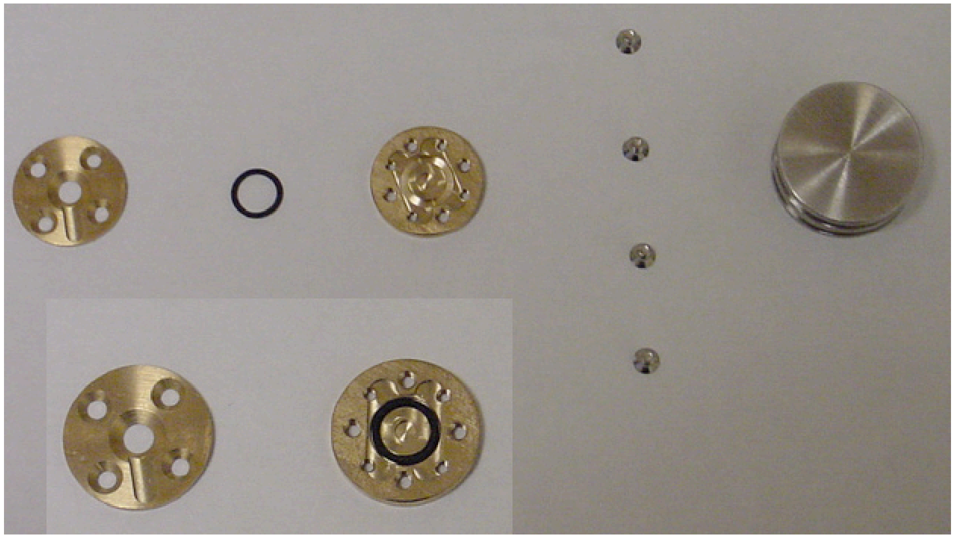


Experimental data from Beamline 7 of the ALS

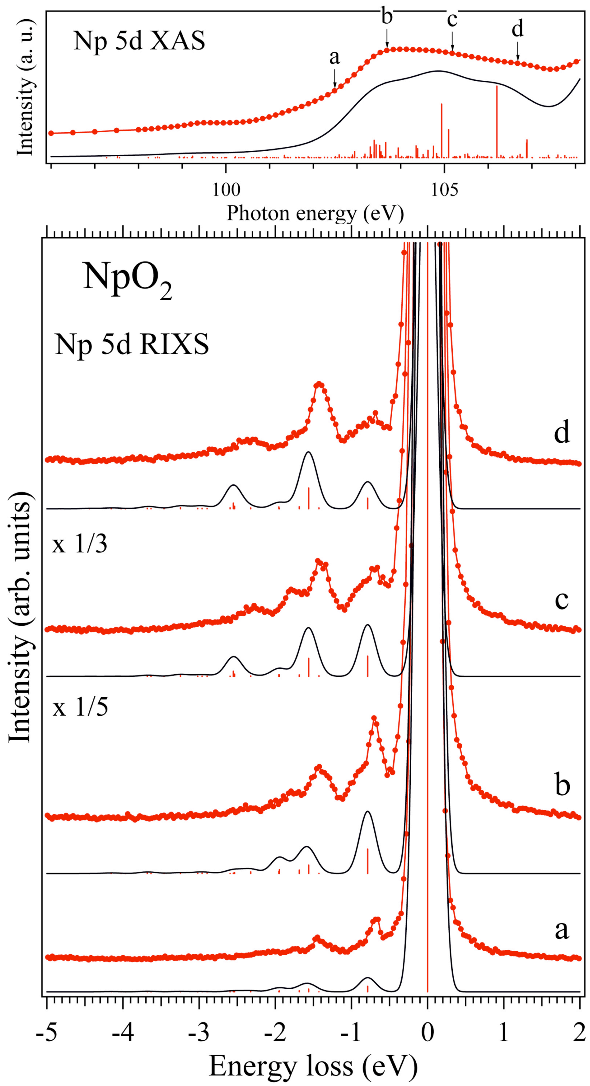
Calculated spectra

Energy-loss features from U 5f excitation

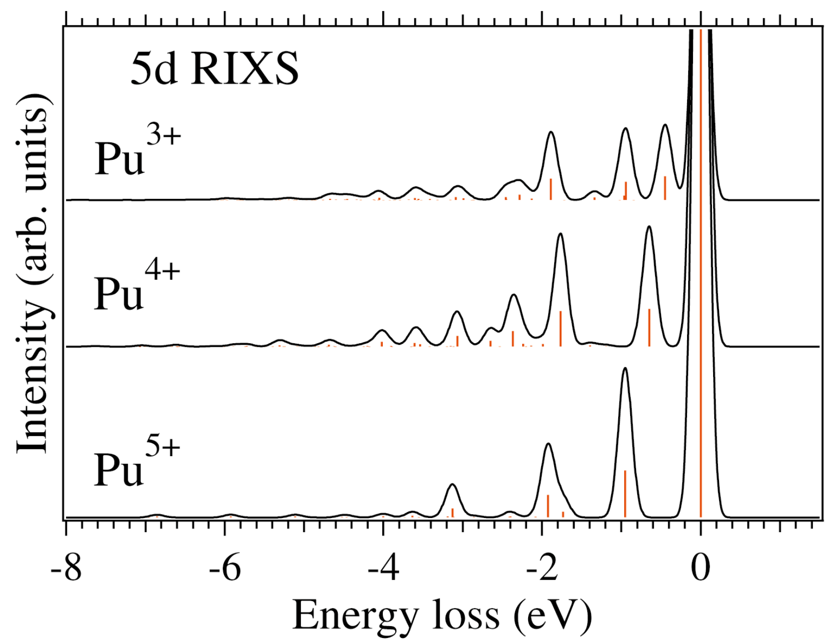
Special XES Sample Holders



X-ray Emission: RIXS
From NpO_2 and Calculated for Pu



Pu Multiplet Calculation at hv= 109.6 eV

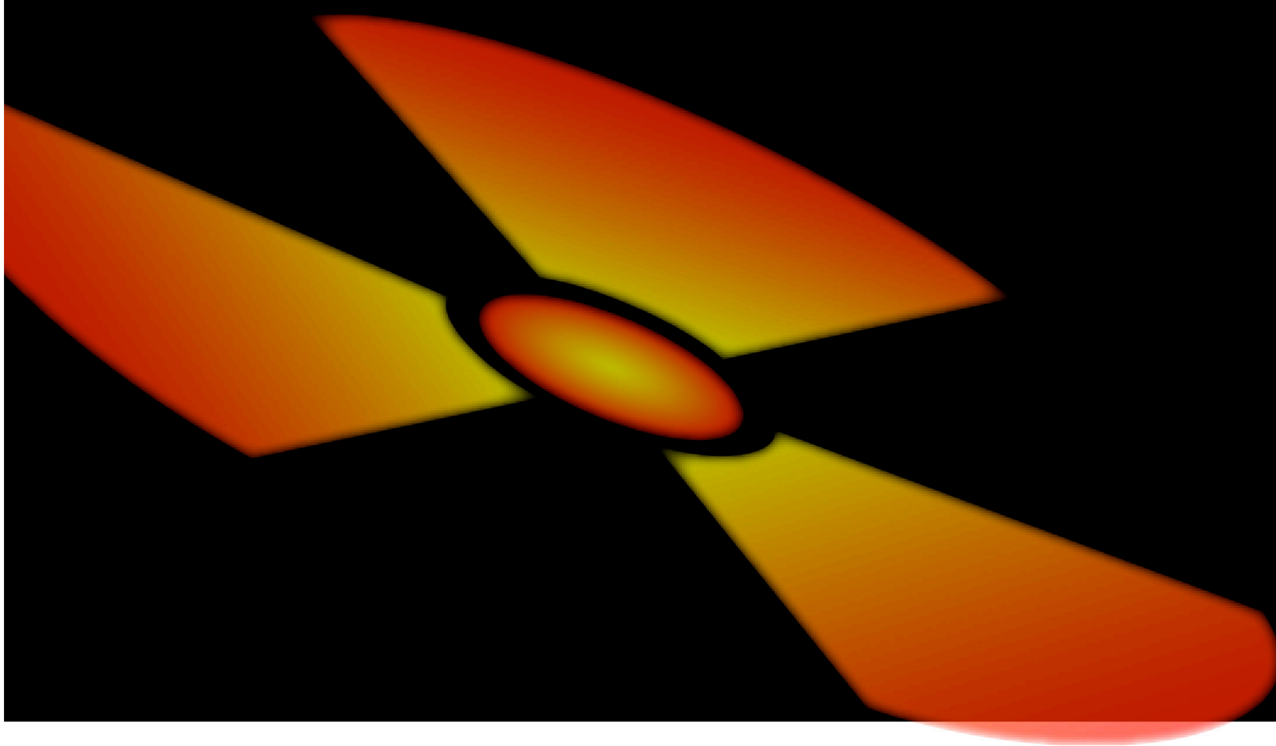


S. M. Butorin et al. (unpublished)

The Nuclear Waste Problem

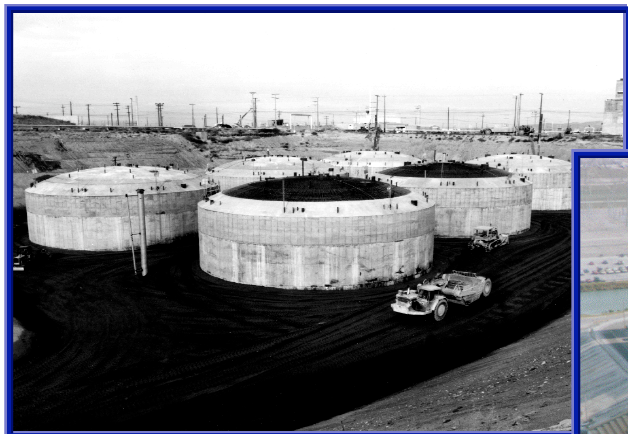
Scientific

Political

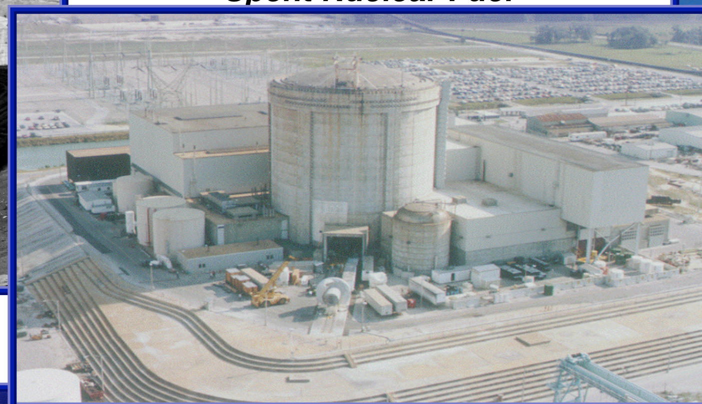


Sources of Nuclear Waste

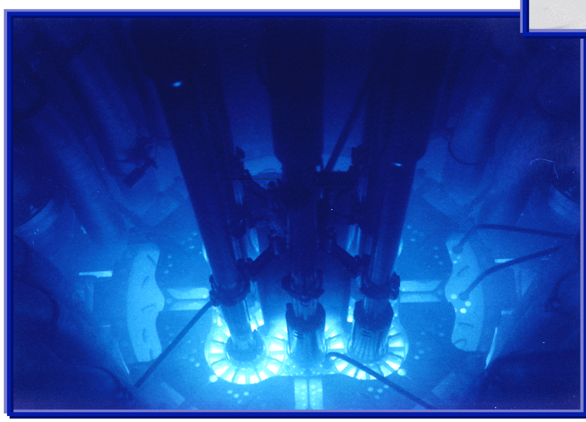
Defense Complex Clean-Up



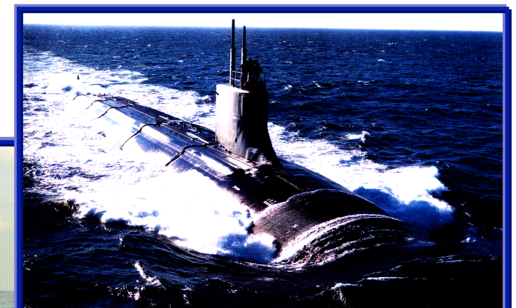
Commercial Spent Nuclear Fuel



Disposition of Surplus Weapons Materials

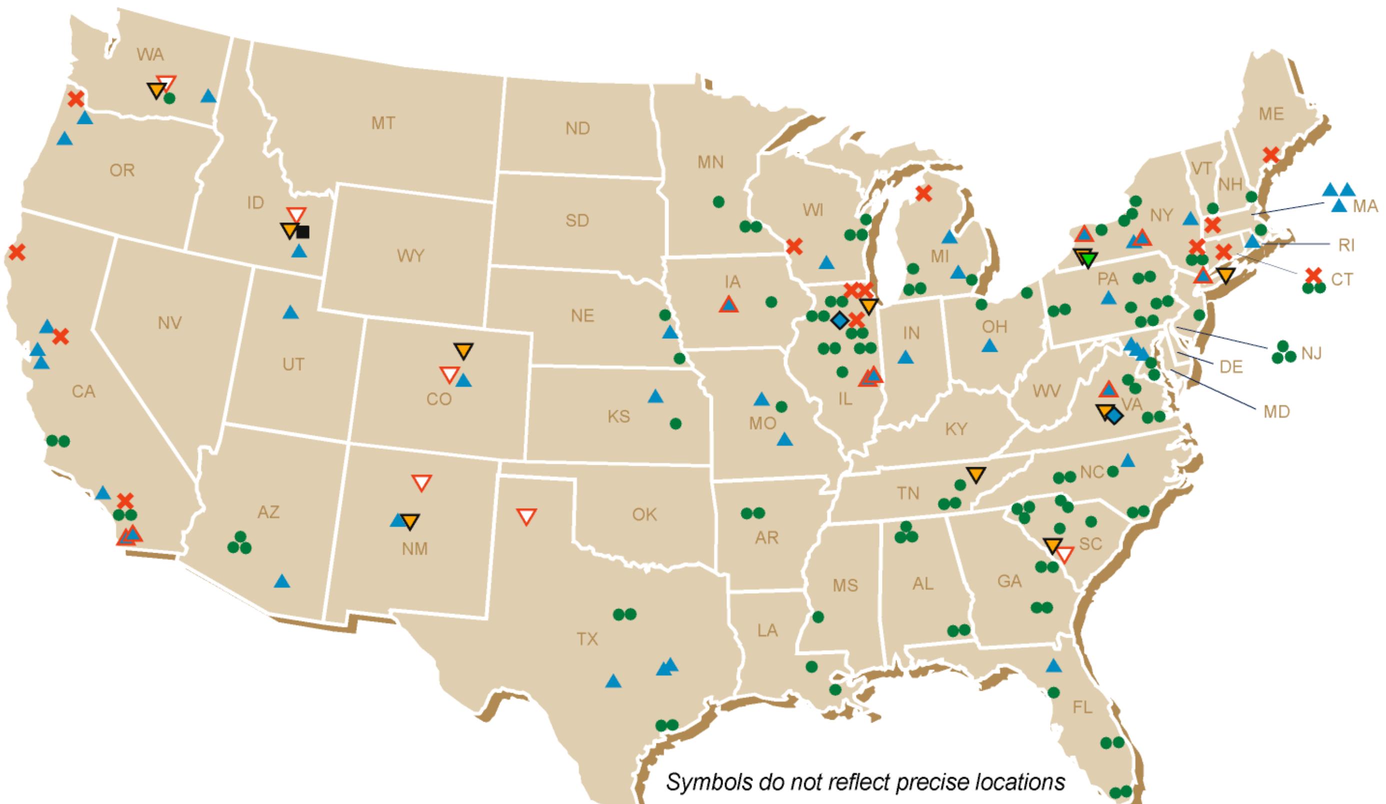


Support of Nonproliferation Initiatives, e.g. Disposal of DOE and Foreign Research Reactor Spent Fuel



Disposition of Naval Reactor Spent Nuclear Fuel

U.S. Storage Locations and Waste Quantities



Current Storage Locations (and Number of Locations)

Commercial Reactors
(72 sites in 33 states), *including:*
- *104 operating reactors, and*
- *14 shutdown reactors with SNF on site*

Research Reactors
(41 sites in 26 states), *including:*
- *36 operating reactors, and*
- *9 shutdown reactors with SNF on site*

Commercial SNF Pool Storage (Away-From-Reactor) (2)

Naval Reactor Fuel (1)

DOE-Owned SNF and HLW (10)

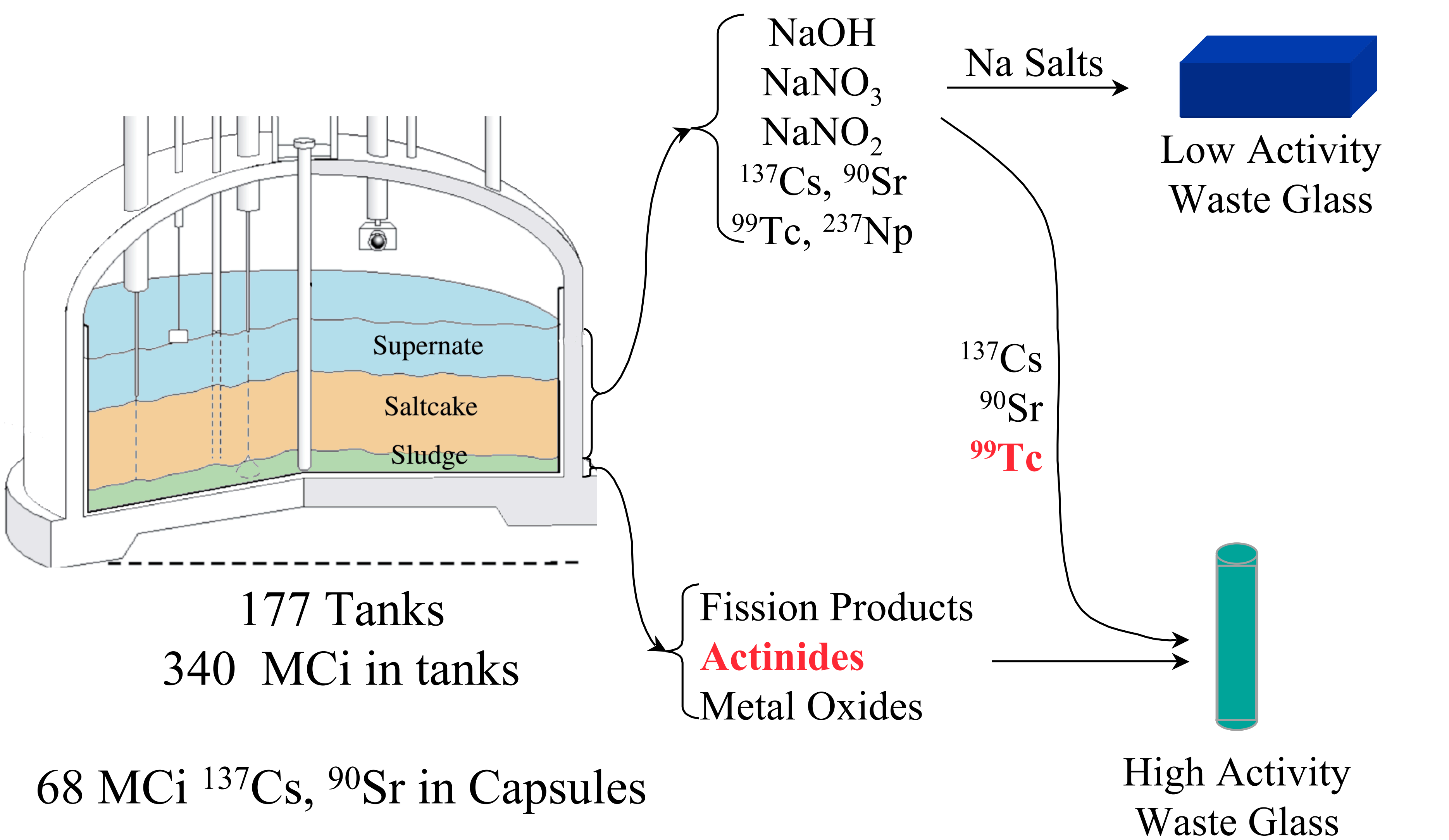
Commercial HLW (1)

Surplus Plutonium (6)

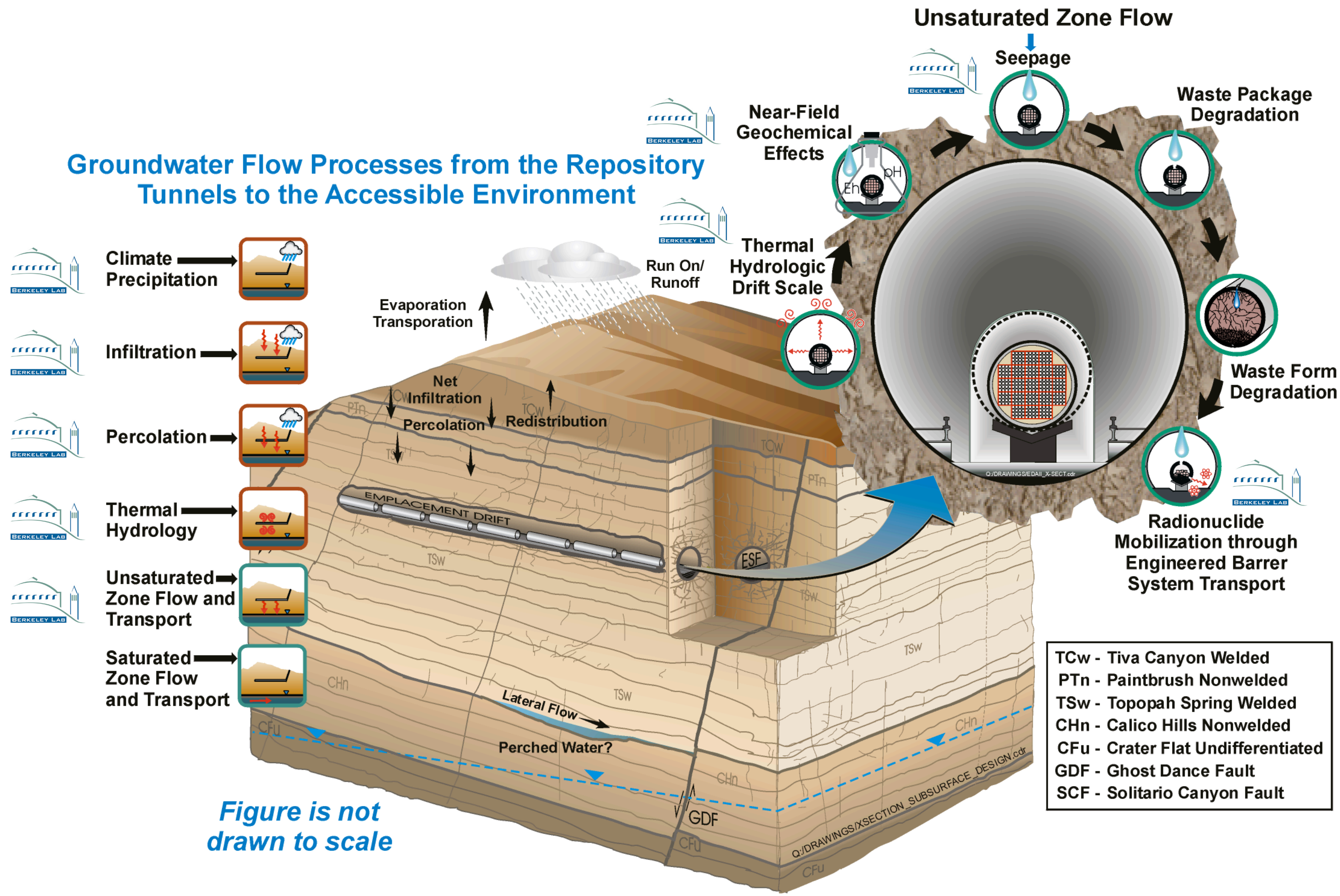
Waste Quantities Projected through 2045
(in Metric Tons, except for HLW)

Commercial SNF	**up to 105,000**
DOE-Owned SNF	**2,500**
including:	
Naval Reactor Fuel	***65***
Foreign Research Fuel	***16***
Surplus Plutonium	**50**
HLW Glass (canisters)	**~22,000**

Hanford Tank Farm Process Schematic

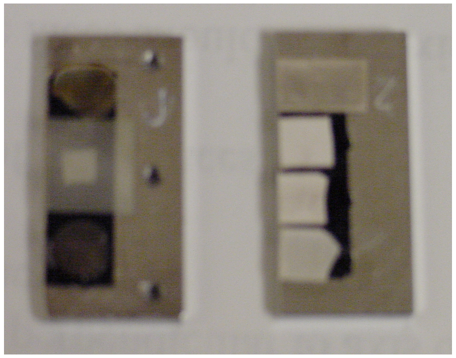


Focus of Current Process Studies



Science of Nuclear Wasteforms

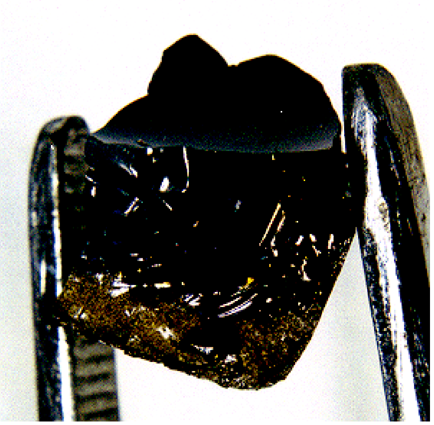
Ceramic materials - pyrochlores



Speciation (oxidation state, structure, form)
Radioactive element loading
Durability and radiation damage
Basis for models and risk assessments

Non-radiaoctive materials at the ALS

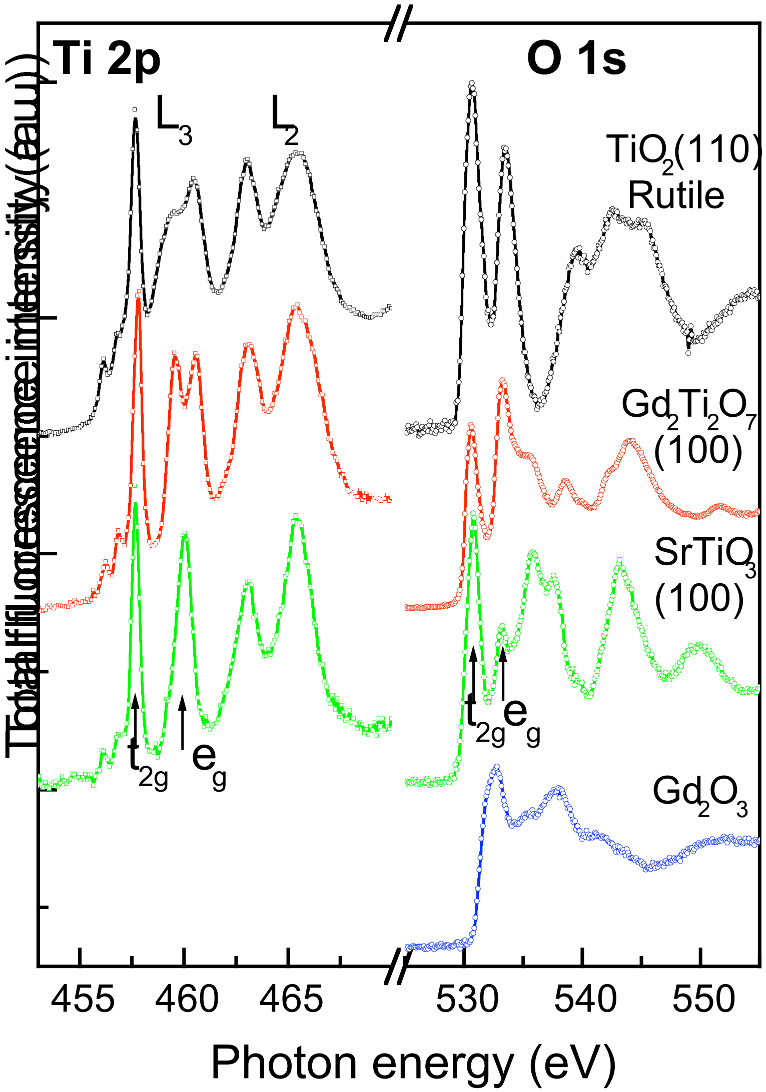
Glasses - mostly borosilicate



Same issues as above

Uranium materials at the ALS

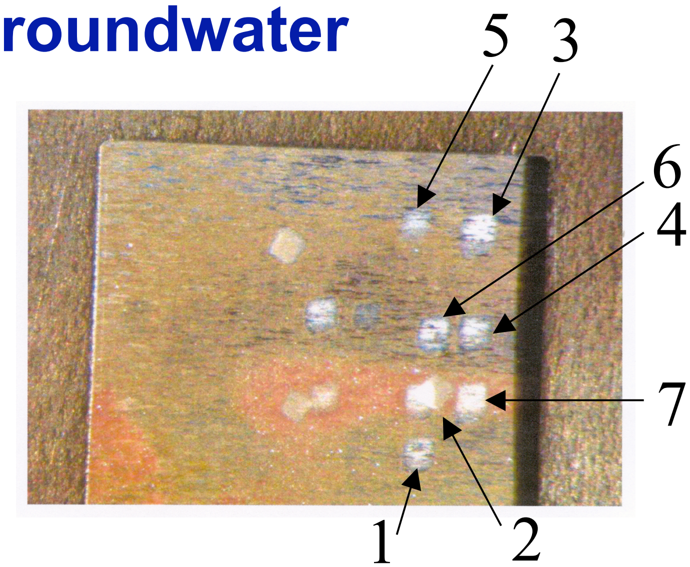
Comparison of the Ti 2p and O 1s NEXAFS from TiO_2, $Gd_2Ti_2O_7$, $SrTiO_3$, and Gd_2O_3



- The crystal field strength ($10Dq=e_g-t_{2g}$) suggests the Ti^{4+} ions in $Gd_2Ti_2O_7$ occupy O_h site symmetry.
- The splitting of e_g states further shows that Ti in $Gd_2Ti_2O_7$ occupies distorted O_h site symmetry.

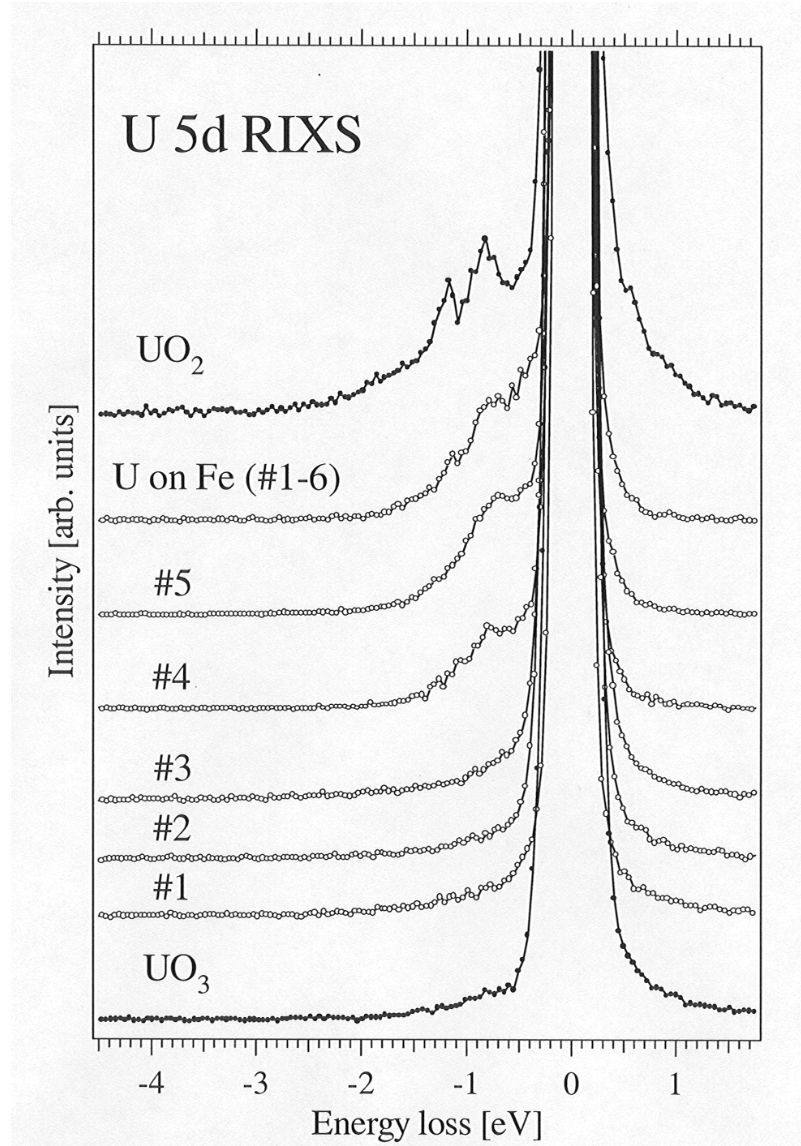
RIXS spectra at hν=101 eV

Contacted for 17 days with 500 ppb U(VI) spiked Allard groundwater



Reduction observed in locations #4-6

ALS BL 7.0 Butorin, Kvashnina, Soroka, Werme, Albinson, Ollila, Nordgren, Guo, Shuh



Specialized Trivalent Separation Ligands (JAERI/LBNL)

Separation of actinide (III) from lanthanide (III)

One of the most important fundamental technologies

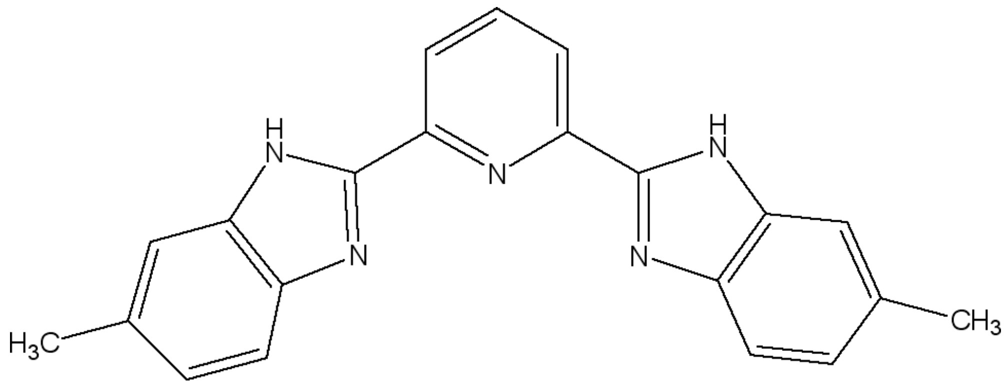
Difficult because the behavior of the ions is similar

Preferential complexation of actinides by soft ligands (ligands that lead to covalent bonding with the metal ion)

Soft donor ligands have been optimized empirically

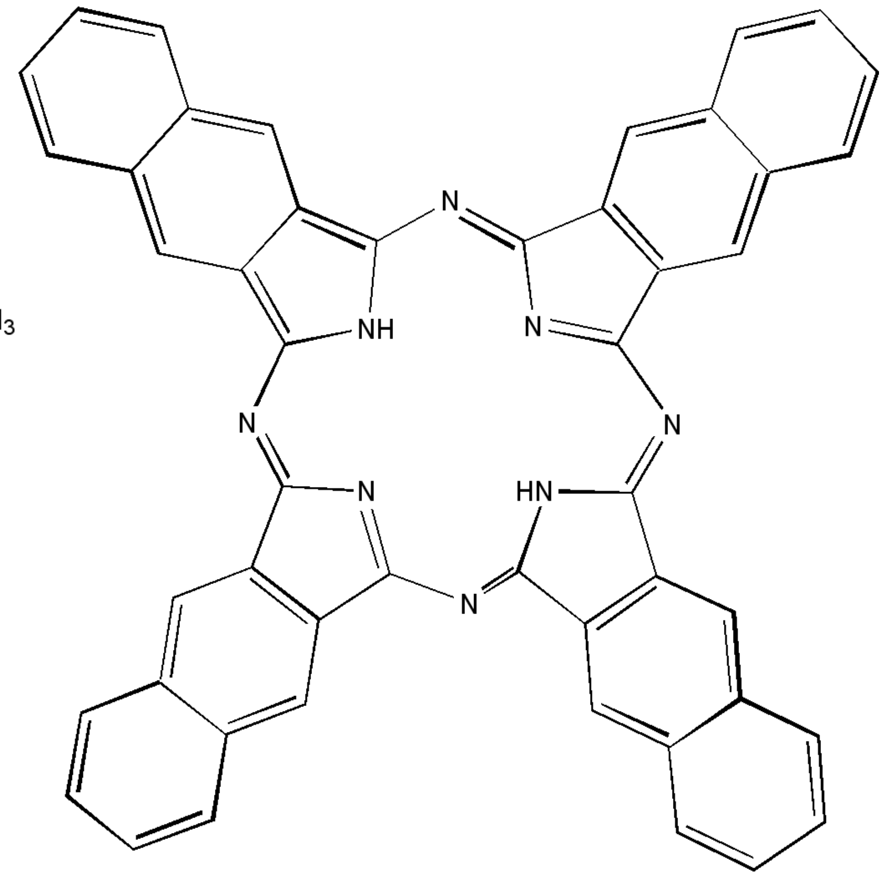
MOLECULAR DESIGN !

Polydentate Aromatic Nitrogen Soft Donor Ligands



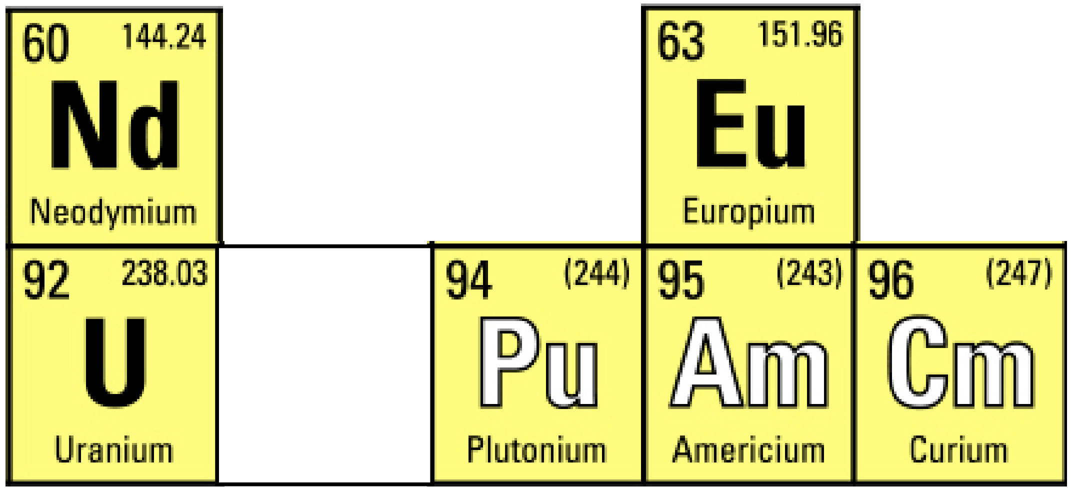
pyridine imidazole derivatives ($-NO_2$, $-CH_3$)

($-NO_2$, $-CH_3$)



phthalocyanine derivatives ($-NO_2$, $-CH_3$)

Experimental Program

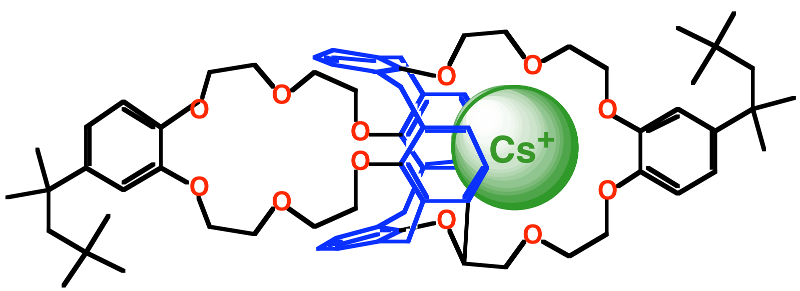


- Chemical Separation Factors (lab experiments)
- NEXAFS - C, N, O K -edges BLs - 6.3.2, 6.3.1
  - lanthanide $M_{IV,V}$ -edges
- XES/RIXS - N K -edge & lanthanide $M_{IV,V}$ -edges BL-8
  - Actinide $O_{IV,V}$ -edges ($5d_{3/2,\,5/2}$) BLs-7, 11

Expertise and Capability: Selective Extraction of the Cs^+ Ion

BOBCalixC6

This molecule features two crown ether loops (red oxygen atoms) on a calixarene frame (in blue). Inside either loop, the Cs^+ ion snugly fits into a cavity bounded on either side by aromatic groups of the calixarene



Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
"BOBCalixC6"
(As complexed with Cs^+ ion)

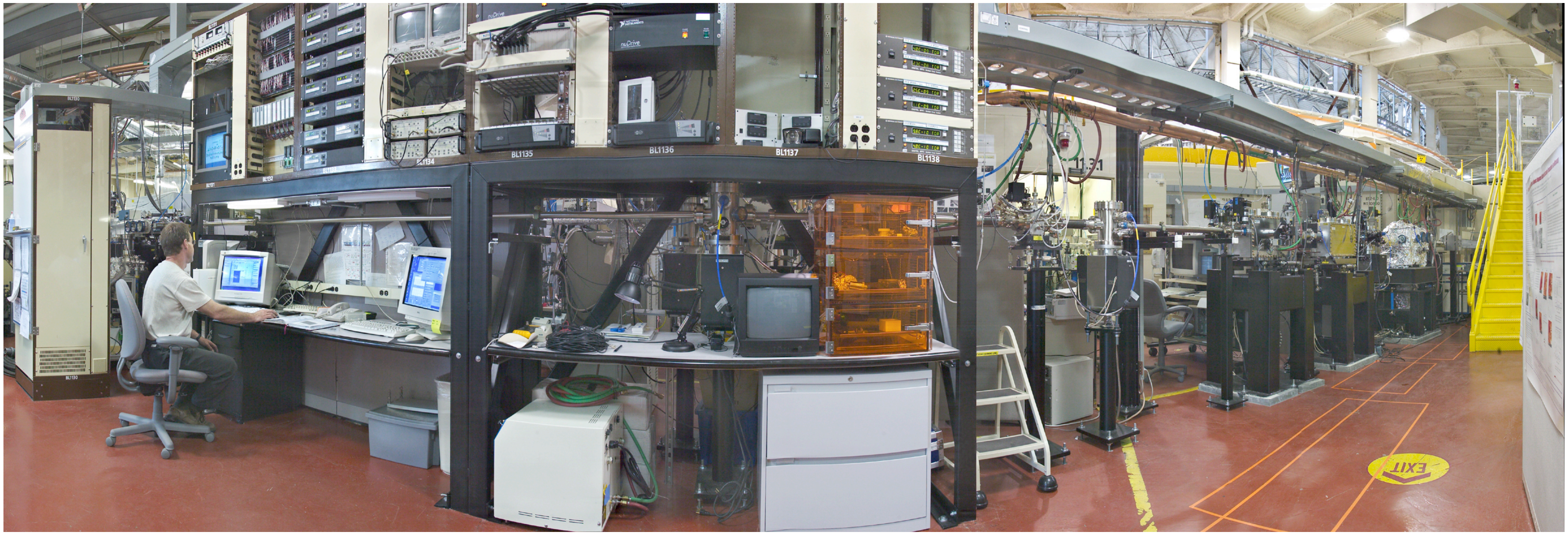
Solvent extraction technology using this molecule chosen for removal of $^{137}Cs^+$ from 31 million gallons of highly radioactive salt waste at Savannah River

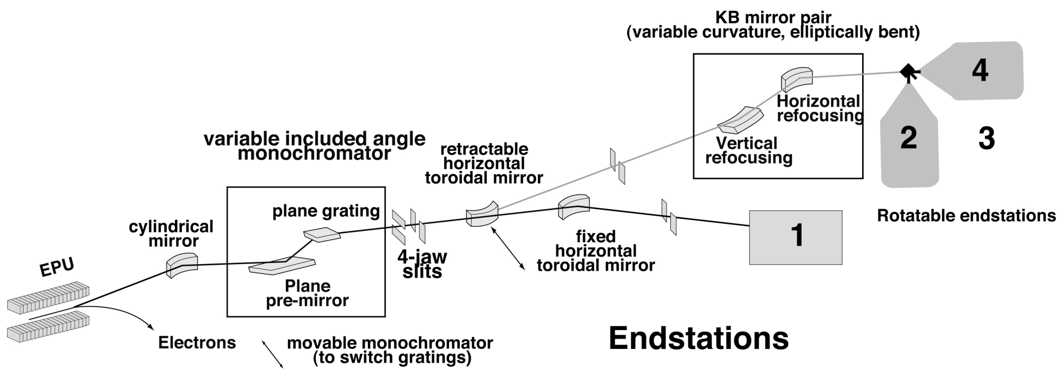
Processing requirements

Remove 99.9975% of the cesium from waste containing an average of only 15 ppm of cesium.

B. Moyer *et al.* ORNL

ALS-MES Beamline 11.0.2





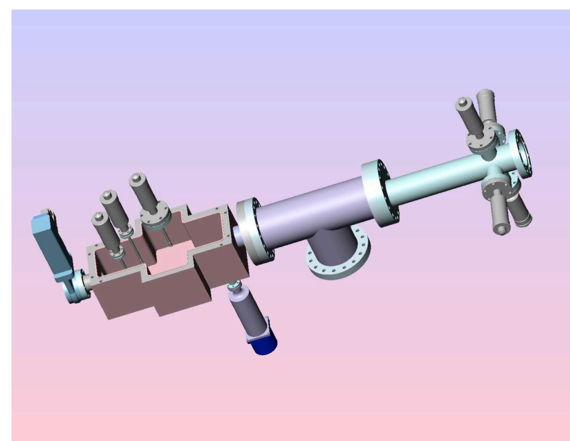
Endstations

1 STXM

2 High pressure photoemission

3 Roll-up experimental chamber

4 Wet spectroscopy



Summary:
A 5f Materials Perspective

XES and RIXS Approaches with Actinides (ANs)

Fundamental information on actinide materials with the need of in-situ sample preparation - sensitive

Electronic and structural characteristics

Versatile (solids, liquids, interface science, clever stuff)

Filled in the soft x-ray scientific gap for ANs (Pu too!)

General Fluorescence Detection Instrumentation and Capabilities:

Important for 5f materials that have not be studied extensively
  Particularly for oxide materials; enables sample environments

Specialized detectors for soft x-rays (normal & high resolution)
  XES, general solid state, and novel instrumentation
  Scanning Transmission X-ray Microscopy (STXM) to SFXM

State-of-the-art Beamlines: BL-11.02 = Intensity, Spot size, Res., P

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